

PRVPATENT- OCH REGISTRERINGSVERKET
Patentavdelningen

BEST AVAILABLE COPY

SE04/1577

RECD 25 NOV 2004

PCT

**Intyg
Certificate**

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.



(71) Sökande Doxa AB, Uppsala SE
Applicant (s)

(21) Patentansökningsnummer 0302844-6
Patent application number

(86) Ingivningsdatum 2003-10-29
Date of filing

Stockholm, 2004-11-04

För Patent- och registreringsverket
For the Patent- and Registration Office


Gunilla Larsson

Avgift
Fee

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

**PATENT- OCH
REGISTRERINGSVERKET
SWEDEN**

Postadress/Adress
Box 5055
S-102 42 STOCKHOLM

Telefon/Phone
+46 8 782 25 00
Vx 08-782 25 00

Telex
17978
PATOREG S

Telefax
+46 8 666 02 86
08-666 02 86

**A SYSTEM FOR A CHEMICALLY BONDED CERAMIC MATERIAL, A
POWDERED MATERIAL AND A HYDRATION LIQUID THEREFORE, AND THE
CERAMIC MATERIAL FORMED THERE FROM**

5 TECHNICAL FIELD

The present invention relates to a system for a chemically bonded ceramic (CBC) material, preferably a dental filling material or an implant material, comprising an aqueous hydration liquid and a powdered material that essentially consists of an inorganic cement system, which powdered material has the capacity following saturation with the hydration liquid to form a complex, chemically bonded material with inorganic as well as organic phases. The invention also relates to the powdered material and the hydration liquid, respectively, as well as the formed ceramic material.

15 STATE OF THE ART AND PROBLEM

The present invention relates to binding agent systems of the hydrating cement system type, in particular cement-based systems that comprise chemically bonded ceramics in the group that consists of aluminates, silicates, phosphates, carbonates, sulphates and combinations thereof, having calcium as the major cat-ion. The invention has been especially developed for biomaterials for dental and orthopaedic applications, both fillers and cements as well as implants including coatings and carriers for drug delivery, but can also be used as fillers in industrial applications in electronics, micro-mechanics etc or in the construction field.

25 For materials, such as dental filling materials and implants, that are to interact with the human body, it is an advantage that the materials are made as bioactive or biocompatible as possible. Other properties that are required for dental filling materials and implants are a good handling ability with simple applicability in a cavity, moulding that permits good shaping ability, hardening/solidification that is sufficiently rapid for filling work without detrimental heat generation and provides serviceability directly following therapy, high hardness and strength, corrosion resistance, good bonding between filling material and biological wall, dimensional stability, radio-opacity, good long time properties and good aesthetics especially regarding dental filling materials. For the purpose of providing a material that fulfils at least most of these required properties, a material has been developed according to what is presented in SE 463,493, SE 502,987, WO 00/21489, WO 01/76534, WO 01/76535, PCT/SE02/01480 and PCT/SE02/01481 e.g.

2003 -10- 2 9

Huvudfaxen Kassan

BRIEF ACCOUNT OF THE INVENTION

The present invention specifically relates to the complex of problems of initial viscosity, dispersing state, setting time, modellability, as well as high strength, viscoelasticity and other mechanical properties, dimensional stability (avoiding shrinking or excessive expansion) and aesthetics, especially regarding dental filling materials, i.e. the problem of being able to optimise a complex property profile in a product and at the same time to optimise the property profile of a CBC system during processing of the same to form the product.

10

Accordingly, the present invention aims at providing a system for CBC materials, preferably biomaterials, having improved controllability concerning its initial viscosity and consistency upon mixing of the powdered material and the hydration liquid of the system and at the same time having improved mechanical properties such as high compressive and bending strength and a sufficiently high E-modulus, a certain viscoelasticity and appropriate hardness, in the hydrated CBC product.

15

Furthermore, the present invention aims at providing such a material having a complex property profile and thereby to provide a powdered material that consists of a cement based system that has the capacity following saturation with a liquid reacting with the powdered material to hydrate and chemically react to a chemically bonded material, which material exhibits both a high degree of compaction, good modellability and minimal dimensional changes upon hardening. Yet another object of the invention is to provide such a material that also exhibits high radio-opacity and high translucency.

20

These and other objectives are attained by the system, the powdered material, the hydration liquid and the ceramic material according to the invention, as defined in the claims.

25

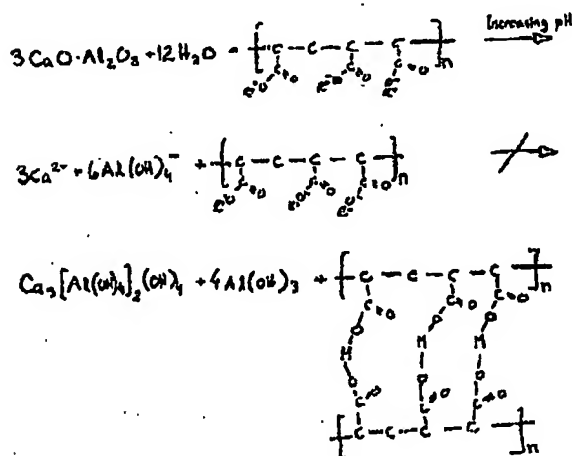
According to the invention, two or more binding phases are activated in the over-all setting/hardening process to optimise initial properties mainly related to rheology as well as end product properties mainly related to mechanical properties.

30

According to one aspect of the invention, the powdered material and/or the hydration liquid comprises an additive of polyacrylic acid and/or a salt thereof or other polycarboxylic acids, co-polymers thereof, or polycarboxylates (i.e. a salt or ester of a polycarboxylic acid).

35

- By the inventive addition of a polycarboxylic acid or a copolymer or a salt or an ester thereof in the powdered material and/or in the hydration liquid, the following reactions take place during dissolving, hydration and polymerisation, here exemplified by a reaction between poly(acrylic-co-maleic acid) and calcium aluminate. R can be any group one ion (i.e. H^+ , Li^+ , Na^+ , K^+ , Rb^+ , preferably H^+ , Na^+ and K^+) or NH_4^+ and M could be a metal ion (e.g. Al^{3+} , Ca^{2+} , Si^{4+}).



10

- The function of the poly acrylic acid or a salt thereof can be divided into cross-linking and dispersing ability. As is understood, in the case with the cross-linking poly acid, the powdered calcium aluminate material is first dissolved in the liquid, where after Ca- and Al-ions cross-links the polyacrylic acid to form a polyacrylate polymer, and other Ca- and Al-ions hydrate to form hydrated calcium aluminate material in a second step. The resulting, hydrated material is a composite of CBC material and a cross-linked polyacrylate polymer.

20

The organic hydrophilic system is not restricted to PAA-systems, but may also be based on other polycarboxylic acids, e.g. poly(maleic acid), poly(itaconic acid) or tricarballic acid) or carboxylates such as phosphate esters. Also, polymers such as PAA/PEG can be used.

25

As is understood, for the function of the dispersing poly acid (e.g. Na-PAMA), the powdered calcium aluminate material is first dissolved in the liquid, where after Ca- and Al-ions form a hydrated calcium aluminate material and in a second step some cross-

2003-10-29

Huvudfaxen Kassar

linking occur with the dispersed poly acid. The resulting, hydrated material is a composite of CBC material and a possible cross-linked polyacrylate polymer.

- 5 Thus two or more binding phases may work at separate time or work over-lapped in the over-all hardening process facilitating the combination of early improved mouldability with high performance end features mainly related to mechanical properties.

DETAILED DESCRIPTION OF THE INVENTION

- 10 The main binder phase of the powdered material consists of a calcium based, basic ceramic powder in the group that consists of aluminates, silicates, phosphates, sulphates and combinations thereof, preferably aluminates. Preferably, the powdered material has a particle size of 0.1 to 20 μm and more preferred 1 to 10 μm .

- 15 The active acids can be introduced either as dried substance together with the inorganic cement or as liquid in the hydration liquid or as a combination of both dry an active acid raw material and a liquid solution of the active acid. For the PAA based systems the introduction in the dry state is preferable.

- 20 Suitably, said polycarboxylic has a molecular weight of 100 – 100,000, preferably 1000 – 50,000 and it is present in an amount of up to 20 %, preferably 1-10 % and most preferred 1-3 % by weight, calculated on the powdered material including any dry additives.

- 25 According to one aspect of the invention, a liquid to powder ratio is 0.1 to 0.7 when mixing the powdered material with the hydration liquid. The solution should have a pH of 1 - 7, preferably 3 – 7 to avoid dissolving of Al^{3+} ions. The pH increases when the polycarboxylic system meets the CA-system, resulting in a basic over-all system at pH > 7. After final hydration the pH approaches neutrality. One problem with pure Glass Ionomer systems is the corrosion resistance sensitivity. The basic CAH system
30 neutralises the initial acidity in the polyacrylic systems.

Said polyacrylic acid or salt thereof is an acid in the group that consists of PAA, Me(I)-PAA, PAMA and Me(I)-PAMA, where

PAA = poly acrylic acid

- 35 PAMA = poly(acrylic-co-maleic acid)

Me(I)-PAMA = poly(acrylic-co-maleic acid) Me(I)-salt

Me(I)-PAA = poly acrylic acid Me(I)-salt

2003 -10- 2 9

Huvudfaxen Kassar

Me(I) = alkali metal ion, e.g. Na, K or Li

In one embodiment of the invention, at least a part or most preferred all of the reactive groups in the polycarboxylic based material bond to the CBC system.

5

In another embodiment of the invention, essentially all reactive groups in said polycarboxylic are neutralised. The neutralisation may be effected e.g. by adding a salt to the reactive groups of the polycarboxylic acid or copolymer. In this embodiment, the polycarboxylic acid acts mainly as a dispersing agent, whereby the initial viscosity of the system, directly upon mixing of the powdered material and the hydration liquid, may be controlled to provide a system that is less viscous than a corresponding system without neutralised polycarboxylic acid, while at the same time the mechanical properties of the hydrated CBC product are maintained or improved.

10

By the present invention, it is possible to reach a viscosity of below 100,000 centipoise, preferably below 10,000 centipoise, directly upon mixing of the powdered material and the hydration liquid, while maintaining a low water content. Hereby, the amount of hydration liquid (water) can be kept beneficially low, while at the same time a viscous blend can be achieved.

20

The system may comprise one or more expansion compensating additives adapted to give the ceramic material dimensionally stable long-term attributes, as is described in WO 00/21489. Other additives and aspects of the system may follow that which is described in SE 463,493, SE 502,987, WO 00/21489, WO 01/76534, WO 01/76535, PCT/SE02/01480 and PCT/SE02/01481, the contents of which are incorporated herein by reference. For example, it is preferred at least for dental filling materials that the system comprises additives and/or is based on raw materials that contribute to translucency of the hydrated material. Also, it is preferred that the system comprises inert dental glass, as an additive in the powdered material, preferably at a content of 5-40 weight-% more preferred 15-35 %. The particle size is critical in establishing high homogeneity. It is preferred that the particle size is 0.1-5 μm , more preferable 0.2 - 2 μm , and most preferable 0.3-0.7 μm . The dental glass may contain low amounts of less stable glass or reactive glass, preferable below 10 % of the glass content. These glasses can preferably contain fluorine and phosphor to yield fluoride ions, which contribute to F-apatite formation.

35

By using granules the w/c ratio (water/cement ratio) can be lower than for the loose powder. The flow-ability of the material is higher when it is granulated. The granules should preferably be of a size below 1 mm, more preferred below 0.5 mm and most preferred below 0.4 mm. The compaction density of the granule, the granule density
5 should be above 35%, preferably above 50 % most preferred above 60%.

By using such highly compacted small granules, the shaping of the material can take place in a subsequent step, without any remaining workability limitations of highly compacted bodies. A facilitated shaping in such a subsequent step, such as kneading,
10 extrusion, tablet throwing, ultrasound etc., can be made while retaining a mobility in the system that has a high final degree of compaction, exceeding 35 %, preferably exceeding 50 %, even more preferred exceeding 60 %.

The principle is based on the fact that a small granule – after granulation of a pre-pressed, highly compacted body – contains several tenths of millions of contact points between particles in the same, which particles are in the micrometer magnitude. When these small granules are pressed together to form new bodies, new contact points arise, which new contact points are not of the same high degree of compaction. The lower degree of compaction in these new contact points results in an improved workability,
20 while the total degree of compaction is only marginally lowered by the lower degree of compaction in the new contact points. This is due to the new contact points only constituting a very slight proportion of the total amount of contact points. Even if for example a thousand new contact points are formed, these contact surfaces will be less than per mille of the total contact surfaces, i.e. they have a very slight influence on the end density, which will be determined by the higher degree of compaction of the granules according to the present invention. Moreover, the contact zones between individual, packed granules will hardly be distinguishable from the other contact points, as the general hardening mechanism for systems according to the invention comprises dissolution of solid material by reaction with water, which leads to the formation of
25 ions, a saturated solution and hydrate precipitation.
30

In a system in which the cement hydrates due to an added liquid, the new contact points will furthermore be filled by hardened phases, which means that the homogeneity increases after the hydration/hardening. By the final degree of compaction being
35 increased in that way, a more dense end product will be obtained, which leads to an increased strength, a possibility to lower the amount of radio-opaque agents and an

2003 -10- 2 9

Huvudfaxen Kassar

easier achieved translucency, at the same time as the workability of the product is very good.

5 According to one aspect of this embodiment, the granules preferably exhibit a degree of compaction above 60 %, even more preferred above 65 % and most preferred above 70 %.

10 Preferably, the granules have a mean size of at least 30 μm , preferably at least 50 μm and even more preferred at least 70 μm , but 250 μm at the most, preferably 200 μm at the most and even more preferred 150 μm at the most, while the powder particles in the granules have a maximal particle size less than 20 μm , preferably less than 10 μm .

15 It should hereby be noted that it is only a very slight proportion of the powder particles that constitute particles having the maximal particle size. The particle size is measured by laser diffraction. The highly compacted granules are manufactured by the powdered material being compacted to the specified degree of compaction, by cold isostatic pressing, tablet pressing of thin layers, hydro-pulse technique or explosion compacting e.g., where after the material compacted accordingly is granulated, for example crushed or torn to granules of the specified size.

20 The system and material according to the invention have the advantages compared to systems/materials such as glass ionomer cements or monomer based filling materials, that it is bioactive, that it has improved strength and that it has long time stability regarding both dimensional aspects, minimised deterioration and high strength compared to Glass Ionomer systems. The material is unique in that it solidifies in at least two steps, i.e. by cross-linking of the polycarboxylic or salt thereof and by

25 hydration. The viscosity of the material can be controlled within wide frames, upon initial mixing of the powdered material and the hydration liquid, from moist granules to an injectable slurry.

EXAMPLE 1

30 A series of tests were performed to investigate the influence of amount of poly acid and the composition of the chemical bonded ceramic on the mechanical properties. The values are compared to commercial glass ionomer cement.

Description of raw materials

35 Calcium aluminate ((CaO)₃(Al_2O_3), (CaO)(Al_2O_3), (CaO)₁₂(Al_2O_3)₇), dental glass filler (Schott), poly acid (PAA = poly acrylic acid Mw=2,000, PAMA = poly(acrylic-co-maleic acid) Mw=3,000, Na-PAMA = poly(acrylic-co-maleic acid) sodium salt

2003 -10- 2 9

Huvudfaxen Kassar

Mw=50,000, Na-PAA = poly acrylic acid sodium salt Mw=5,100). Glass ionomer cement, Fuji II (GC-corp).

Description of tests5 *Test a) to w) investigated:*

- a) Hardness and compressive yield strength of Fuji II, glass ionomer cement, reference.
- b) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 1 wt.% PAA.
- 10 c) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% PAA
- d) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 14 wt.% PAA
- e) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 1 wt.% PAMA
- 15 f) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% PAMA
- g) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 14 wt.% PAMA
- 20 h) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 1 wt.% Na-PAMA
- i) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% Na-PAMA
- j) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 14 wt.% Na-PAMA
- 25 k) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 1 wt.% Na-PAA
- l) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% Na-PAA
- 30 m) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 14 wt.% Na-PAA
- n) Hardness and compressive yield strength of $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ mixed with 35 vol.% dental glass and 7 wt.% PAA
- o) Hardness and compressive yield strength of $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ mixed with 35 vol.% dental glass and 7 wt.% PAMA
- 35 p) Hardness and compressive yield strength of $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ mixed with 35 vol.% dental glass and 7 wt.% Na-PAMA

2003 -10- 2 9

Huvudfaxen Kassen

- q) Hardness and compressive yield strength of $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ mixed with 35 vol.% dental glass and 7 wt.% Na-PAA
- r) Hardness and compressive yield strength of $(\text{CaO})_3(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% PAA
- 5 s) Hardness and compressive yield strength of $(\text{CaO})_3(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% PAMA
- t) Hardness and compressive yield strength of $(\text{CaO})_3(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% Na-PAMA
- 10 u) Hardness and compressive yield strength of $(\text{CaO})_3(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 7 wt.% Na-PAA
- v) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ (mean grain size 5 μm) mixed with 35 vol.% dental glass and 1 wt.% Na-PAMA
- w) Hardness and compressive yield strength of $(\text{CaO})(\text{Al}_2\text{O}_3)$ (mean grain size 10 μm) mixed with 35 vol.% dental glass and 1 wt.% Na-PAMA

15

The calcium aluminate phases were synthesised via a sintering process where first CaO and Al_2O_3 was mixed to the desired composition and then sintered at elevated temperature for 6 hours. The formed calcium aluminate lumps were crushed and jet-milled to the desired grain size distribution. The dental glass, calcium aluminate and poly acid was mixed with acetone and Si_3N_4 marbles for 14 hours to obtain the desired homogeneity. The samples in test b-w) were blended to a water to cement ratio of 0.4 in 5 ml jars and rotated at 500 rpm for 30 seconds. Samples for hardness and compressive yield strength (sample size according to ISO-9917) were made from the formed paste. Glass ionomer samples were made according to the manufactures

20 instructions. All samples were stored in phosphate buffer solution for 7 days before measuring. Before measuring all samples were polished with down to 0.25 μm diamond paste on cloths. The compressive yield strength was measured on a Zwick Roell Z005 universal mechanical test rig. For each composition 20 samples were tested and the mean value reported in table 1.1. The hardness was measured as Vickers hardness using

25 200 grams load on the same number of samples as in the compressive yield strength test.

30

2003 -10- 2 9

Huvudfaxen Kassen

Table 1.1 Hardness and compressive yield strength for test a)-w)

Test	Hardness VHN	Compressive yield strength MPa
A	60	110
B	130	172
C	110	151
D	98	122
E	127	169
F	109	152
G	100	139
H	140	191
I	135	171
J	115	152
K	137	195
L	129	168
M	112	150
N	105	154
O	107	149
P	134	182
Q	133	190
R	106	141
S	108	152
T	131	192
U	135	197
V	141	201
W	129	182

- 5 The results showed that by mixing poly acid with calcium aluminate and dental glass a higher hardness and compressive yield strength compared to glass ionomer cements could be achieved. More poly acid and larger grain size decreases the hardness and the compressive strength. Poly acids with sodium salt give better mechanical properties than the pure poly acids.

EXAMPLE 2

A series of tests were performed to investigate the influence of amount and molecular weight of poly acid, the ratio between water and cement and the composition of the chemical bonded ceramic on handling properties. The values are compared to a commercial calcium aluminate based dental material (DoxaDent, Doxa AB).

Description of raw materials

Calcium aluminate ($\text{CaO}(\text{Al}_2\text{O}_3)$), dental glass filler (Schott), poly acid (PAA = poly acrylic acid ($\text{Mw} = 2000, 13000, 45000$), PAMA = poly(acrylic-co-maleic acid) ($\text{Mw} = 3400, 25000, 37000$), Na-PAMA = poly(acrylic-co-maleic acid) sodium salt ($\text{Mw} = 2100, 23000, 44000$), Na-PAA = poly acrylic acid sodium salt ($\text{Mw} = 2600, 17000, 36000$)).

Description of tests

Test a) to m) investigated:

- a) Mouldability of DoxaDent.
- b) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% PAA and a water to cement ratio of 0.2.
- c) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% PAA and a water to cement ratio of 0.3.
- d) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% PAA and a water to cement ratio of 0.4.
- e) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% PAMA and a water to cement ratio of 0.2.
- f) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% PAMA and a water to cement ratio of 0.3.
- g) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% PAMA and a water to cement ratio of 0.4.
- h) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% Na-PAMA and a water to cement ratio of 0.2.
- i) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% Na-PAMA and a water to cement ratio of 0.3.
- j) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% Na-PAMA and a water to cement ratio of 0.4.
- k) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% Na-PAA and a water to cement ratio of 0.2.

P1774

Hynell Patenttjänst

Ink. t. Patent- och reg.verket

12

2003 -10- 2 9

Huvudföreläsnings Kassa

l) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% Na-PAA and a water to cement ratio of 0.3.

m) Mouldability of $(\text{CaO})(\text{Al}_2\text{O}_3)$ mixed with 35 vol.% dental glass and 5 wt.% Na-PAA and a water to cement ratio of 0.4.

5

The calcium aluminate phases were synthesised via a sintering process where first CaO and Al_2O_3 was mixed to the desired composition and then sintered at elevated temperature for 6 hours. The formed calcium aluminate lumps were crushed and jet-milled to a mean grain size of 1.5 μm and a maximum grain size of 9 μm . The dental glass, calcium aluminate and poly acid was mixed with acetone and Si_3N_4 marbles for 14 hours to obtain the desired homogeneity. The samples in test b-w) were blended to the desired water to cement ratio in 5 ml jars and rotated at 500 rpm for 30 seconds. DoxaDent samples were made according to the manufactures instructions. The mouldability was determined by placing the mixed paste in a syringe and ejecting the paste via a 1 mm needle with hand force. The feasibility of the mixtures to be ejected are presented in table 2.1.

10

15

Table 2.1 Mouldability of test a) to m)

Test	Mouldability
A	No
B	No
C	Yes
D	Yes
E	No
F	Yes
G	Yes
H	No
I	Yes
J	Yes
K	No
L	Yes
M	Yes

20 The results show that for a water to cement ratio above 0.2 the mixtures are ejectable from a syringe.

EXAMPLE 3

A series of tests were performed to investigate the influence of poly acid on the acid erosion resistance.. The values are compared to a commercial glass ionomer cement (Fuji II) and to a commercial calcium aluminate based dental material (DoxaDent, Doxa AB).

Description of raw materials

Calcium aluminate (CaO)(Al_2O_3), dental glass filler (Schott), Na-PAMA = poly(acrylic-co-maleic acid) sodium salt.

Description of tests

Test a) to c) investigated:

- a) the acid erosion of Fuji II
- b) the acid erosion of DoxaDent
- c) the acid erosion of (CaO)(Al_2O_3) mixed with 35 vol.% dental glass and 5 wt.% Na-PAMA and a water to cement ratio of 0.4.

The calcium aluminate phases were synthesised via a sintering process where first CaO and Al_2O_3 was mixed to the desired composition and then sintered at elevated temperature for 6 hours. The formed calcium aluminate lumps were crushed and jet-milled to a mean grain size of 3 μm and a maximum grain size of 9 μm . The dental glass, calcium aluminate and poly acid was mixed with acetone and Si_3N_4 marbles for 14 hours to obtain the desired homogeneity. The samples in test c) were blended to the desired water to cement ratio in 5 ml jars and rotated at 500 rpm for 30 seconds. DoxaDent and Fuji II samples were made according to the manufactures instructions. The acid erosion was measured according to ISO-9917.

The results showed that the tests in b and c exhibited an acid erosion of below 0.01 mm/h whereas the glass ionomer cement showed a acid erosion of 0.1 mm/h. Thus the results show that addition of poly acid to calcium aluminate does not reduce its acid resistance.

The invention is not limited to the embodiments described, but can be varied within the scope of the claims.

Ink. t. Patent- och reg.verket

-10- 2 9

Huvudfaxen Kassar

CLAIMS

1. A system for a chemically bonded ceramic material, comprising an aqueous hydration liquid and a powdered material comprising a first binder phase, which powdered material has the capacity following saturation with the liquid reacting with said first binder phase to hydrate to a chemically bonded ceramic material, characterised in that the system also comprises a second, non-ceramic binder phase, which second binder phase has a different initiation time for setting and/or a different setting rate than the initiation time for hydration and the hydration rate, respectively, of said first binder phase, and in that the system provides for an ion interaction between the hydration reactions and setting reactions of the first binder phase and the second binder phase, respectively.
2. A system according to claim 1, characterised in that the chemically bonded ceramic material is a material in the group that consists of aluminates, silicates, phosphates, sulphates and combinations thereof, preferably having cations in the group that consists of Ca, Sr and Ba, calcium aluminate cements being most preferred, in which case the first binder phase preferably has a composition between the phases $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, most preferably about $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, optionally in glass phase.
3. A system according to claim 1 or 2, characterised in that said second binder phase comprises a polycarboxylic acid or a copolymer or a salt or an ester thereof.
4. A system according to any one of claims 1 - 3, characterised in that it has a viscosity below 100,000 cP, preferably below 10,000 cP, directly upon mixing of the powdered material and the hydration liquid, at a low water to cement ratio (W/C), preferably at W/C below 0.46, most preferred below 0.40.
5. A powdered material comprising a first binder phase essentially consisting of a cement system, which powdered material has the capacity following saturation with a hydration liquid reacting with said first binder phase to hydrate to a chemically bonded ceramic material, characterised in that said powdered material also comprises an additive of a second, non-ceramic binder phase, which second binder phase has a different initiation time for setting and/or a different setting rate than the initiation time for hydration and the hydration rate,

2003 -10- 2 9

Huvudfaxen Kassar

respectively, of said first binder phase, and in that the hydration liquid together with the powdered material provides for an ion interaction between the hydration reactions and setting reactions of the first binder phase and the second binder phase, respectively.

5

6. A powdered material according to claim 5, characterised in that that the chemically bonded ceramic material is a material in the group that consists of aluminates, silicates, phosphates, sulphates and combinations thereof, preferably having cations in the group that consists of Ca, Sr and Ba, calcium aluminate cements being most preferred, in which case the first binder phase preferably has a composition between the phases $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, most preferably about $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, optionally in glass phase.
- 10
7. A powdered material according to claim 5 or 6, characterised in that said second binder phase comprises a polycarboxylic acid or a copolymer or a salt or an ester thereof.
- 15
8. A powdered material according to claim 7, characterised in that at least a part or most preferred all the reactive groups of said polycarboxylic acid or salt thereof bond to the chemically bonded ceramic material.
- 20
9. A powdered material according to any one of claims 7 to 8, characterised in that said polycarboxylic acid or copolymer or salt or ester thereof is a substance in the group that consists of poly acrylic acid, poly(acrylic-co-maleic acid), poly(itaconic acid), tricarballic acid; copolymers, salts and esters thereof; and combinations thereof.
- 25
10. A powdered material according to any one of claims 7 to 9, characterised in that said polycarboxylic acid or copolymer or salt or ester thereof has a molecular weight of 100 – 100,000, preferably 1000 – 50,000 and that it is present in an amount of up to 20 %, preferably 1-10 % and most preferred 1-3 % by weight, calculated on the powdered material including any additives.
- 30
11. A powdered material according to any one of claims 5 to 10, characterised in that it contains an inert phase additive, preferably including dental glass and preferably at a content of 5-40 weight-% more preferred 15-35 %.
- 35

2003 -10- 2 9

Huvudfaxen Kassar

12. A powdered material according to claim 11, characterised in that said inert phase additive has a particle size of 0.1-5 μm , more preferably 0.2 - 2 μm , and most preferably 0.3-0.7 μm .
- 5 13. A powdered material according to claim 11 or 12, characterised in that that said inert phase comprises low amounts of less stable phases or reactive phases including glasses, preferably below 10 % of the inert phase content, which less stable phases or reactive phases preferably comprise fluoride and/or phosphor.
- 10 14. A powdered material according to any one of claims 5 to 13, characterised in that it has the form of granules, preferably of a size below 1 mm, more preferred below 0.5 mm and most preferred below 0.4 mm and having a granule compaction density above 35 %, preferably above 50 % most preferred above 60%.
- 15 15. An aqueous hydration liquid for a powdered material comprising a first binder phase essentially consisting of a cement system, which powdered material has the capacity following saturation with the hydration liquid reacting with said first binder phase to hydrate to a chemically bonded ceramic material, characterised in that said hydration liquid comprises an additive of a second, non-ceramic binder phase, which second binder phase has a different initiation time for setting and/or a different setting rate than the initiation time for hydration and the hydration rate, respectively, of said first binder phase, and in that the hydration liquid together with the powdered material provides for an ion interaction between the hydration reactions and setting reactions of the first binder phase and the second binder phase, respectively.
- 20 16. An aqueous hydration liquid according to claim 15, characterised in that said second binder phase comprises a polycarboxylic acid or a copolymer or a salt or an ester thereof.
- 25 17. An aqueous hydration liquid according to claim 16, characterised in that at least a part or most preferred all of the reactive groups of said polycarboxylic acid or salt thereof bond to the chemically bonded ceramic material.
- 30 35

- 5 18. An aqueous hydration liquid according to any one of claims 16 - 17,
characterised in that said polycarboxylic acid or copolymer or salt or ester
thereof is a substance in the group that consists of poly acrylic acid,
poly(acrylic-co-maleic acid), poly(itaconic acid), tricarballic acid; copolymers,
salts and esters thereof; and combinations thereof.
- 10 19. An aqueous hydration liquid according to any one of claims 16 - 18,
characterised in that said polycarboxylic acid or copolymer or salt or ester
thereof has a molecular weight of 100 - 100,000, preferably 1000 - 50,000.
20. An aqueous hydration liquid according to any one of claims 15 - 19,
characterised in that it has a pH of 1-7, preferably > 3, before the
hydration and setting reactions.
- 15 21. A chemically bonded ceramic material, the binder phase of which essentially
consisting of an inorganic cement phase, which ceramic material is in situ
formed on a substrate or in a cavity, characterised in that said material
also comprises an in situ formed phase of polyacrylate polymer or co-polymer.

Ink. t. Patent- och reg.verket

2003-10-29

ABSTRACT

Huvudfaxen Kassan

5 A system for a chemically bonded ceramic material, comprising an aqueous hydration liquid and a powdered material comprising a first binder phase, which powdered material has the capacity following saturation with the liquid reacting with said first binder phase to hydrate to a chemically bonded ceramic material. The system also comprises a second, non-ceramic binder phase, which second binder phase has a different initiation time for setting and/or a different setting rate than the initiation time for hydration and the hydration rate, respectively, of said first binder phase, and the
10 system provides for an ion interaction between the hydration reactions and setting reactions of the first binder phase and the second binder phase, respectively. The invention also relates to the powdered material and the hydration liquid, respectively, as well as the formed ceramic material.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.